

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
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1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE		3. DATES COVERED (From - To)	
		New Reprint		-	
4. TITLE AND SUBTITLE Thermal Stability of Fluorinated Polydienes Synthesized by Addition of Difluorocarbene			5a. CONTRACT NUMBER		
			W911NF-10-1-0297		
			5b. GRANT NUMBER		
6. AUTHORS Tianzi Huang, Xiaojun Wang, Thomas Malmgren, Kunlun Hong, Jimmy W. Mays			5c. PROGRAM ELEMENT NUMBER		
			611102		
			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Tennessee at Knoxville 1534 White Avenue Knoxville, TN 37996 -1529			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 57790-CH.4		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
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15. SUBJECT TERMS fluoropolymers, glass transition, thermal properties, degradation, thermogravimetric analysis					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Jimmy Mays
UU	UU	UU	UU		19b. TELEPHONE NUMBER 865-974-0747

Report Title

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REPORT DOCUMENTATION PAGE (SF298) (Continuation Sheet)

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ARO Report Number 57790.4-CH
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Block 13: Supplementary Note

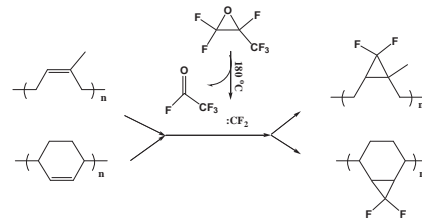
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Thermal Stability of Fluorinated Polydienes Synthesized by Addition of Difluorocarbene

Tianzi Huang, Xiaojun Wang, Thomas Malmgren, Kunlun Hong, Jimmy W. Mays*

Linear PCHD and polyisoprenes with different microstructures and molecular weights are synthesized and chemically modified to improve their thermal and chemical stability by forming a three-membered ring structure containing two C–F bonds. Pyrolysis of these fluorinated polydienes proceeds through a two-stage decomposition involving chain scission, crosslinking, dehydrogenation, and dehalogenation. The pyrolysis leads to graphite-like residues, whereas their polydiene precursors decompose completely under the same conditions. The fluorination of PCHD enhances its thermal stability. The stronger C–F bond along with high strain of the three-membered ring structure and formation of relatively stable free radicals play an important role in the thermal stability of fluorinated polydienes.



1. Introduction

Their unsaturated structures render polydienes less stable than other polymers under harsh chemical (oxygen aging, solvent swelling, moisture, etc.) and physical (heat, solar radiation, etc.) conditions and thus limit their applications. Post-polymerization modification is thus an important method used to alter the chemical nature of polydienes. Such modifications can result in an enhancement of their properties and extension of their applications. Along with hydrogenation, halogenation including fluorination, has been studied to improve the performance of polymers by introducing C–F bonds.^[1] The high electronegativity of fluorine leads to strong, polar C–F bonding, resulting in better thermal stability and chemical inertness. Since the ionic radius of fluorine is small, the C–F bonds have limited ability to polarize, which leads to a low index of refraction

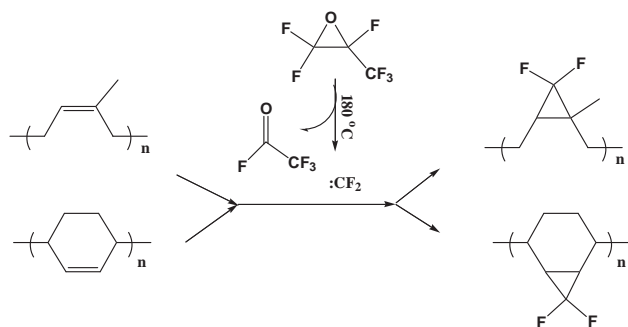
(low dielectric constant) and modest intermolecular interactions (low surface tension).^[2]

Fluorination of polydienes by different approaches has been previously reported and it has been reviewed recently.^[3] For example, Lodge and Hillmyer^[4] described radical grafting of perfluoroalkyl iodides. Hydrosilylation of perfluoroalkylsilanes also has been used to modify polydienes.^[5] It was recently reported that a mild, selective, and quantitative fluorination of polydienes could be achieved by in situ generated difluorocarbenes (:CF₂) from thermolysis of hexafluoropropylene oxide.^[6] We also used this method to react the residual carbon–carbon double bonds of poly(1,3-cyclohexadiene) (PCHD) with difluorocarbene.^[7]

The addition of difluorocarbene to the double bonds leads to a three-membered ring structure containing two C–F bonds. The fluorination reaction schemes for 1,4-polyisoprene and 1,4-PCHD are shown in Scheme 1.

Unlike fluoropolymers, such as polytetrafluoroethylene in which the majority of the chemical bonds of the polymers are C–F bonds, fluorinated polymers obtained by chemical modification of hydrocarbon polymers have fewer C–F bonds, while retaining different types of chemical bonds present in their precursors. These latter bonds will exhibit the same, or similar, responses when they are exposed to chemical and thermal treatment as

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Scheme 1. Fluorination of polydienes with in situ generated difluorocarbene.

the chemical bonds in their precursors. Therefore, the chemical and thermal stabilities of fluorinated polymers are affected by the fluorocarbon bonds as well as the hydrocarbon (and possibly other) bonds. Studies until today show that fluorinated polydienes synthesized by addition of difluorocarbenes to their double bonds have much higher glass transition temperatures (T_g) as compared with their polydiene precursors.^[6,7] The preliminary results of thermal treatment of fluorinated PCHD under a nitrogen purge revealed higher temperatures for the onset of decomposition, higher temperatures for the maximum rate of decomposition, and greater residue after thermal treatment as compared with their polydiene precursors.^[7] In this paper, detailed thermal stability studies on several fluorinated polydienes and their precursors are reported.

2. Experimental Section

The synthesis, fluorination, and characterization of linear PCHD with controlled molecular weights, narrow polydispersities, and varied microstructures were previously reported.^[7] Linear PCHD samples were hydrogenated using *p*-toluenesulfonylhydrazide (TSH) in toluene by gently refluxing for 16 h under an argon atmosphere. The degree of functionalization was characterized in deuterated chloroform on a Varian Mercury 300 MHz NMR instrument. Polyisoprene with 93% 1,4-microstructure made by anionic polymerization was fluorinated with difluorocarbene, as reported by Ren et al.^[4,6]

Thermal stability analyses and pyrolysis studies were performed on a thermogravimetric analysis instrument (TGA Q50, TA Instrument Inc.) at a heating rate of 10 °C min⁻¹ under a nitrogen or air flow of 60 mL min⁻¹. The onset temperature of decomposition was determined by the tangent of the weight loss curve. The temperature of maximum rate of decomposition was determined by the peak in the derivative of the weight loss curve. Isothermal treatment was performed by heating the sample to a desired temperature at a heating rate of 10 °C min⁻¹ and then holding the temperature constant for a period of time that equals the time needed to heat the sample up to 600 °C at the same heating rate. Differential scanning calorimetry (DSC)

was performed under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹, with the second heating being chosen for analysis in order to eliminate the thermal history of the sample.

Fourier transform infrared (FT-IR) spectra were obtained using a Bio-Rad FTS 6000 instrument, via either transmission mode (400–4000 cm⁻¹), using films cast from solution on silicon wafers or pellets pressed from mixtures with KBr, or in attenuated total reflectance (ATR) mode (700–4000 cm⁻¹) using solid samples. The spectra were analyzed on the basis of published spectra^[8] and the standard infrared spectra of model organic molecules published by Sadtler Research Laboratories. The elemental analysis was done by Galbraith Laboratory Inc. (Knoxville, TN).

3. Results and Discussion

During thermal treatment (pyrolysis), chemical bonds may break either homolytically or heterolytically, and bonds may reform, which leads to polymer chain decomposition and structural rearrangement. The breaking and reforming of chemical bonds are affected by the strength of the chemical bonds, the kinetic and thermodynamic competition between products generated, and the experimental conditions such as heating rate, sample size, atmosphere, etc.^[9,10] In this study, we thus maintained all the conditions the same or at least minimized changes.

Generally, when polymer pyrolysis occurs under vacuum or under inert gas flow, the polymer chains go through three main types of decomposition processes: chain scission, chain crosslinking, and chain-stripping reactions.^[9] These three different decomposition processes lead to different decomposition products. Chain scission generates volatile materials such as monomer, dimer, or oligomers. Chain crosslinking generates less volatile materials but more unsaturated structures, such as aromatized materials or char. Chain stripping generates small volatile molecules by the loss of substituents (side group reactions) without affecting the main chain of the polymer. These three types of decomposition processes may occur individually or in combination during pyrolysis.

To understand the thermal stability of fluorinated polymers obtained by addition reactions of difluorocarbenes, three different fluorinated polydiene samples, two hydrogenated polydiene samples, and their polydiene precursors were investigated. The chemical nature, molecular weights, and polydispersity indices, degrees of functionality, and T_g of fluorinated, and hydrogenated polydiene samples, and their precursors are summarized in Table 1. All the polydiene precursors were synthesized via anionic polymerization to obtain controlled microstructure, molecular weights, and narrow molecular weight distributions. The fluorination and characterization methods were reported elsewhere.^[7] The hydrogenation of PCHD samples was performed in toluene with TSH and characterized as for the fluorinated samples.

■ Table 1. Characteristics of polydienes before and after chemical modification.

Sample	Nature of polymer	Molecular weight [g mol ⁻¹]	PDI	Degree of saturation [mol%]	T _g [°C]
A	PCHD (high 1,4-)	16 200	1.12	—	120
B	PCHD (50/50 1,4/1,2-)	19 700	1.12	—	138
FA	fluorinated PCHD	20 300	1.24	91	199
FB	fluorinated PCHD	15 400	1.12	71	229
HA	hydrogenated PCHD	—	—	100	204
HB	hydrogenated PCHD	—	—	95	228
C	PI (high 1,4-)	76 800	1.09	—	-61 ^{a)}
FC	fluorinated PI	99 500	1.27	98	43 ^{a)}

^{a)}Literature value.^[6]

3.1. Pyrolysis of PCHD

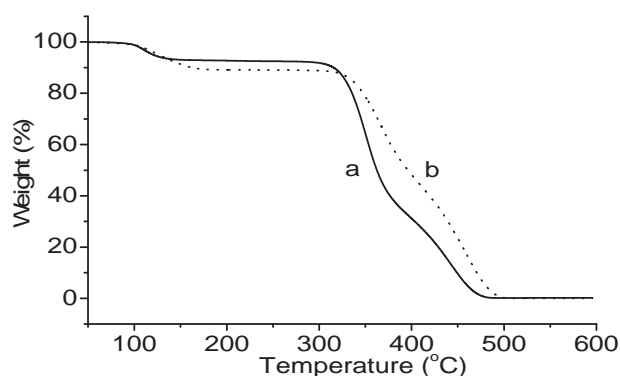
Weight losses (decompositions, under N₂) over three different temperature ranges were observed for PCHD samples. The first weight loss of around 10 wt% was observed between 75–125 °C for 1,4-PCHD with high-1,4-microstructure (≈95%). Continued heating led to a second weight loss starting at 328 °C, which reached a maximum decomposition rate at 350 °C. A third temperature of maximum decomposition rate was observed at 440 °C, which resulted in complete decomposition. The microstructure of PCHD did not significantly affect the pyrolysis behavior. The linear sample with about 50% 1,4-microstructure showed similar weight loss patterns to the high 1,4-PCHD, but the temperatures of maximum decomposition rate are higher (365 and 460 °C, respectively) (Figure 1). The decomposition profiles match previously reported data very well.^[11]

The weight loss at low temperature was initially believed to be caused by release of solvent that is “trapped in” the condensed polymer during polymer recovery process after polymerization because it was located in the vicinity of the glass transition of PCHD and the temperature seems to be too low for chain scission. However,

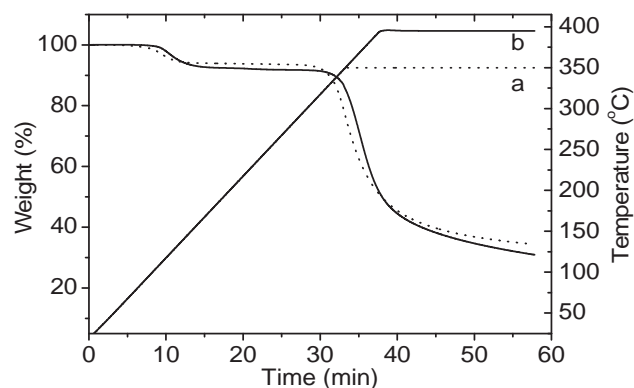
more detailed studies found that the low temperature weight loss was attributed to degradation at the PCHD chain end.^[12] The mechanism of this unzipping of the chain ends is not clear. Thermal treatment of PCHD in bulk at 200 °C under argon eliminated this weight loss on subsequent reheating,^[12] whereas thermal treatment in benzene with inhibitor (2,6-di-*tert*-butyl-4-methylphenol, ≈0.067 wt%) at 180 °C under argon in a Parr reactor, followed by precipitation, did not eliminate this weight loss.

Isothermal pyrolysis of PCHD with high 1,4-microstructure at the second maximum decomposition temperature (350 °C) led to a yellowish solid material. The total weight loss was around 65%–70% after either isothermal treatment at 350 °C for 25 min or at 395 °C for 20.5 min (Figure 2). The weight of the residue remained constant after pyrolysis, which indicates that a thermally stable material was formed. The residue was not soluble in common solvents.

The structure of the residue was analyzed via elemental analysis and FT-IR. Compared with its linear precursor, the residue has similar carbon and hydrogen contents



■ Figure 1. TGA curves for linear PCHD: (a) high-1,4-PCHD and (b) 50/50 1,4/1,2-PCHD.



■ Figure 2. Isothermal pyrolysis of linear PCHD at 350 °C for 25 min (a, dotted line) and at 395 °C for 20.5 min (b, solid line).

Table 2. The elemental analysis results and empirical formula of samples before and after pyrolysis.

Sample	Elemental analysis			Recovered weight [%]	Empirical formula
	C [%]	H [%]	F [%]		
A	89.18	9.44	–	0	C ₆ H _{7.6} ^{a)}
A-py@ 395	89.36	9.51	–	30–35	C ₆ H _{7.6}
FA	65.72	6.32	27.94	0	C ₇ H _{8.1} F _{1.9} ^{b)}
FA-py@395	80.99	6.30	13.00	15–20	C ₇ H _{6.5} F _{0.7}
FA-py@600	94.24	3.80	0.34	12–16	C ₇ H _{3.4} F _{0.0}
FC	60.20	6.25	35.33	0	C ₆ H _{7.3} F _{2.2} ^{c)}
FC-py@340	78.61	7.33	15.78	70–75	C ₆ H _{6.7} F _{0.8}
FC-py@600	91.32	3.37	1.08	20–23	C ₆ H _{2.6} F _{0.0}

^{a)}Theoretical formula for linear PCHD is C₆H₈; ^{b)}Theoretical formula for fluorinated PCHD is C₇H₈F₂; ^{c)}Theoretical formula for fluorinated polyisoprene is C₆H₈F₂.

and empirical formula (Table 2, A: precursor; A-py@395: residue) but exhibited a different FT-IR spectrum (Figure 3). The typical signals after pyrolysis at 395 °C for 20.5 min, such as the C–H stretching (3018 cm^{−1}), the C–H in-plane deformation (1312 cm^{−1}) and out-plane deformation (974 cm^{−1}) from the olefin groups (–CH=CH–) in PCHD, and the breathing of cyclohexene-like ring systems (1069 cm^{−1}) decreased or disappeared; while C–H stretching (2922 and 2858 cm^{−1}) and deformation (1445 cm^{−1}) from –CH₂– were observed in all spectra. The changes in peak profile of typical C=C stretching (1646 cm^{−1}) suggested the emergence of different types of carbon–carbon double bonds, such as unconjugated, conjugated, and aromatic, after pyrolysis. A higher *T*_g of 152 °C after pyrolysis as compared with one of 120 °C for the precursor indicates the more limited mobility of chain segments of the former polymers.

All the characterization data lead us to conclude that the thermal pyrolysis of PCHD involves two kinds of decomposition mechanisms. One mechanism is chain scission to lose volatile materials^[11] (monomer, dimer, and oligomers) that were carried out by N₂ flow during heating; and the other mechanism is crosslinking caused by addition to double bonds or coupling of free radicals generated by homolytic bond cleavage. Chain crosslinking results in a three-dimensional structure as indicated by the higher *T*_g of the residue and insolubility in common solvent, leading to enhanced thermal stability as well as retarded decomposition. The competition between chain scission and crosslinking is related to the conversion, thickness of the sample, and the flow rate of nitrogen. Chain rearrangement also occurred during this isothermal pyrolysis based on changes in the FT-IR spectra.

3.2. Pyrolysis of Hydrogenated PCHD

Crosslinking during thermal pyrolysis of PCHD is mainly attributed to the presence of carbon–carbon double bonds and the generation of radicals. This assumption was verified by thermal pyrolysis of hydrogenated PCHD, in which the double bonds were saturated by hydrogenation. Linear PCHDs with different microstructures were hydrogenated using TSH in toluene and the degree of hydrogenation was characterized via ¹H NMR (Table 1). DSC characterization shows that hydrogenation leads to a much higher *T*_g (Table 1, HA and HB).

As expected, hydrogenation enhanced the thermal stability of PCHD, which led to an elevated onset temperature of decomposition. The TGA curves of two hydrogenated PCHD samples with different microstructures are shown in Figure 4. Hydrogenated linear PCHD with 95% 1,4-microstructure started to decompose at 440 °C and the sample completely decomposed over a narrow temperature range with maximum decomposition rate at 445 °C.

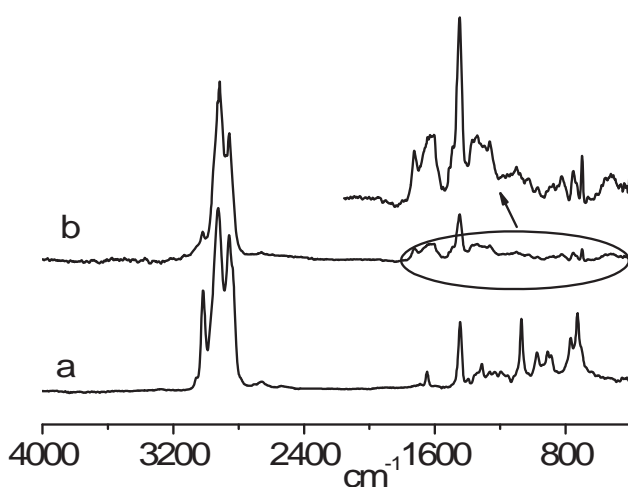


Figure 3. FTIR spectra of linear PCHD (a) before and (b) after pyrolysis at 395 °C for 20.5 min.

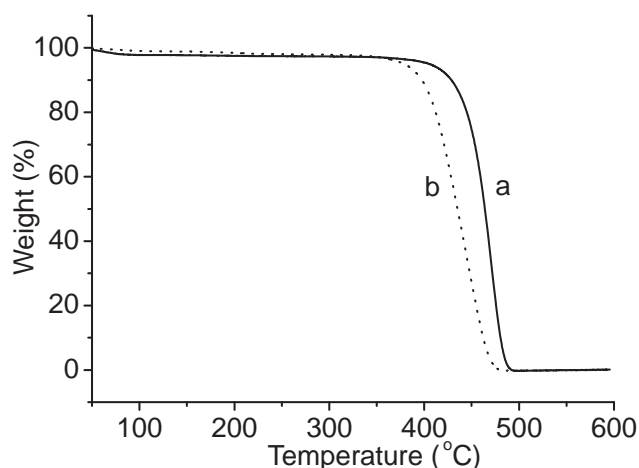


Figure 4. TGA curves of hydrogenated PCHD from precursors of high-1,4-PCHD (a, solid line) and 50/50 1,4/1,2-PCHD (b, dotted line).

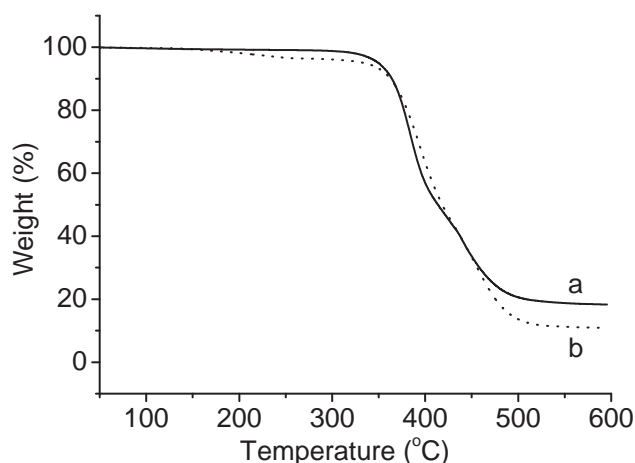


Figure 5. TGA curves of fluorinated PCHD from precursors of high-1,4-PCHD (a, solid line) and 50/50 1,4/1,2-PCHD (b, dotted line).

The weight loss at low temperature (75–125 °C) observed in PCHD was not observed after hydrogenation. The hydrogenated PCHD with 50% 1,4-microstructure started to decompose at 400 °C and the temperature of maximum decomposition was 470 °C. The lack of two stages of pyrolysis above 300 °C is attributed to the absence of double bonds in the hydrogenated PCHD, which resulted in only chain scission without crosslinking.

3.3. Pyrolysis of Fluorinated PCHD

Although fluorination of linear PCHD with in situ generated difluorocarbene saturated the double bonds, the pyrolysis of fluorinated PCHD under an inert atmosphere still shows decompositions over two different temperature ranges (Figure 5). The weight loss at low temperature (75–125 °C) observed in PCHD was eliminated by fluorination. The decomposition of fluorinated PCHD started around 360 °C, and reached a maximum decomposition rate at 395 °C, which is 50 °C higher than for its PCHD precursor. Weight loss continued above 400 °C and stopped around 500 °C yielding a shiny, graphite-like residues with a weight percentage of 4.8 to 16.5% depending on the degree of fluorination.^[7] The microstructure of PCHD did not have much influence on the thermal decomposition process (Figure 5). For fluorinated PCHD with 50% 1,4-microstructure, a similar TGA curve was observed and the relatively low weight percentage of residue was attributed to the relatively lower degree of fluorination (71 mol%) (Table 1, FA, FB; Figure 5).

Oxygen lowered the thermal decomposition temperature and led to complete decomposition of fluorinated PCHD. Figure 6 shows fluorinated PCHD decomposed under different atmospheres using the same heating rate. The onset decomposition temperature of fluorinated PCHD under air flow was around 310 °C and complete

decomposition occurred around 600 °C. The TGA trace also shows two stages of weight loss, which suggests that the thermal decomposition of fluorinated PCHD pyrolyzed under air flow proceeds through a similar process to pyrolysis under a nitrogen flow.

Fluorinated PCHDs were isothermally pyrolyzed at 395 °C, which is the first temperature of maximum decomposition rate under nitrogen (Figure 7). The weight loss was around 80–85 wt% when the sample was held isothermally at 395 °C for 20.5 min. The residual material was graphite-like and insoluble in common solvents. The weight loss was larger than that for PCHD isothermally pyrolyzed at the same temperature and over the same time period. Although fluorinated PCHD has a higher onset decomposition temperature (more thermally

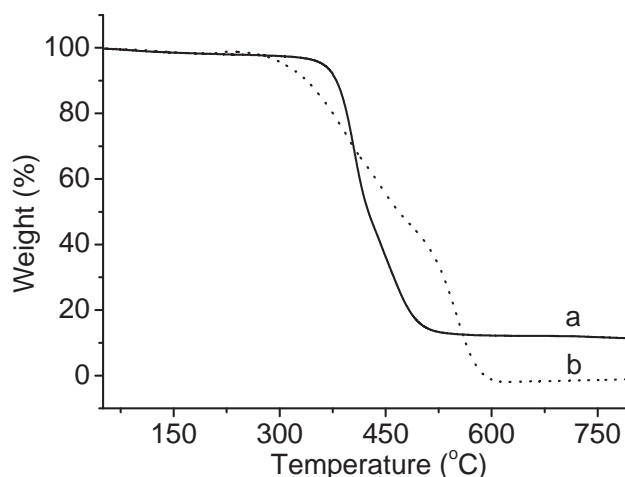


Figure 6. TGA curves of fluorinated PCHD from precursors of high-1,4-PCHD under different atmosphere of nitrogen (a, solid line) and air (b, dotted line).

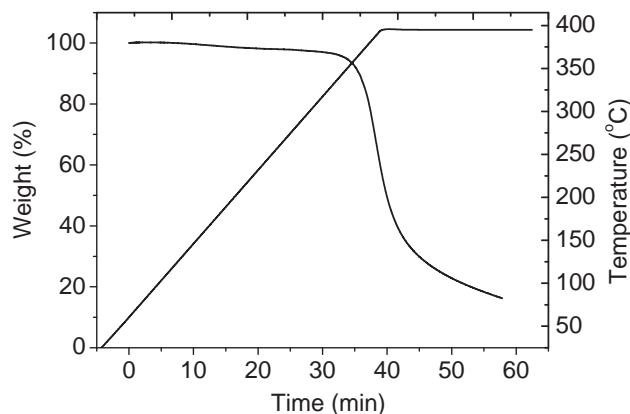


Figure 7. Isothermal pyrolysis of fluorinated PCHD (395 °C, 20.5 min).

stable at low temperature), it tended to decompose completely after decomposition started. The reduced level of carbon–carbon double bonds in fluorinated PCHD (≈ 9 mol%, sample FA in Table 1) leads to a lower degree of crosslinking during isothermal pyrolysis; therefore, the formation of a thermally stable, three-dimensional network is less likely.

DSC characterization did not show obvious glass transition type heat capacity changes for the isothermally pyrolyzed residue. Elemental analysis showed relatively higher ratios of carbon to hydrogen and carbon to fluorine (FA-py@395 in Table 2). The FT-IR spectra (Figure 8) shows the weakening of the C–F stretching (1100 – 1350 cm^{-1}) (Figure 8b), and the increasing C–H stretching (3044 cm^{-1}) on unsaturated carbons. The aromatic C=C stretching (1601 cm^{-1}) and C–H out-of-plane deformation (745 , 810 , and 875 cm^{-1}) are clearly observed.

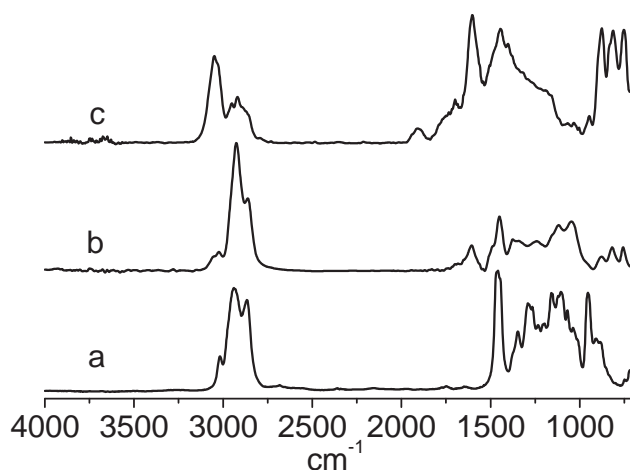


Figure 8. FT-IR spectra of fluorinated PCHD before (a) and after (b) pyrolysis (395 °C, 20.5 min) and (c) heated up to 600 °C.

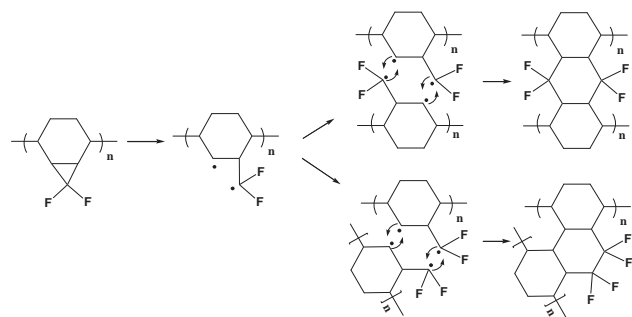
Elemental analysis and FT-IR characterization suggest that not only crosslinking but also dehalogenation occurred during the isothermal pyrolysis, which led to an unsaturated carbon system with less fluorine and hydrogen. Continuous pyrolysis up to 600 °C caused more extensive dehydrogenation and dehalogenation and led to more highly aromatized materials. The FT-IR spectrum shows much stronger C–H stretching (3044 cm^{-1}) on unsaturated carbons, much stronger aromatized C–H out-of-plane deformation (745 , 810 , and 875 cm^{-1}), and much stronger C=C stretching of the aromatic type (1601 cm^{-1}) together with non-conjugated type (1694 cm^{-1}) or even vinyl type (1906 cm^{-1}). Elemental analysis shows the loss of most fluorine atoms and more hydrogen, which agrees with the FT-IR results very well (sample FA-py@600 in Table 2).

To eliminate the effect of carbon–carbon double bonds, the remaining carbon–carbon double bonds in fluorinated PCHD were saturated by hydrogenation with TSH in toluene. ^1H NMR characterization proved the success of this process. Hydrogenation did increase the onset decomposition temperature, but two stages of decomposition pattern were still observed, as in fluorinated PCHD. The hydrogen saturated fluorinated PCHD has a lower decomposition onset decomposition temperature as compared with hydrogenated PCHD, and the two-stage decomposition suggests that chain crosslinking occurred even though there were no carbon–carbon double bonds left in this specific sample. The comparison of the pyrolysis behaviors of fluorinated PCHD, hydrogenated PCHD, hydrogenated and fluorinated PCHD, leads to the conclusion that the presence of a three-membered ring structure could trigger chain decomposition and cause crosslinking during pyrolysis by processes discussed below.

The high strain in the three-membered ring and the polarized C–F bonds made the C–CF₂ bonds in the ring structure much weaker than other C–C bonds. The homolytic breakage of the C–CF₂ bonds generates two free radicals, which can trigger a much more thorough decomposition. The decomposition of fluorinated PCHD consists of chain scissions to generate volatile low-molecular-weight materials (monomer, dimer, etc.), chain crosslinking, and dehalogenation. A possible chain crosslinking mechanism is shown in Scheme 2.

3.4. Pyrolysis of Fluorinated Polyisoprene

The assumption of thermal cleavage of the three-membered ring that triggers polymer decomposition was substantiated by the thermal decomposition study of fluorinated polyisoprene synthesized by similar addition of *in situ* generated difluorocarbenes. The TGA trace taken during pyrolysis of polyisoprene under a nitrogen atmosphere with a heating rate of 10 °C min^{-1} shows a rapid, smooth



Scheme 2. Possible crosslinking mechanisms during thermal pyrolysis of fluorinated PCHD.

weight loss curve beginning at 350 °C with a maximum decomposition rate at 380 °C (Figure 9). Previous studies found that the pyrolysis of polyisoprene under vacuum generates mostly isoprene monomers and dimers (such as 1-methyl-4-isopropenylcyclohexene, and its isomers) via a mechanism of chain scission to form two free radicals, and backbiting of the free radical involving one or two monomer units.^[13,14] The fluorinated polyisoprene has a lower onset temperature of decomposition at 325 °C, and undergoes a two-stage decomposition (maximum decomposition temperatures of 340 and 450 °C, respectively (Figure 9). A graphite-like residue of 20 wt% was obtained after pyrolysis up to 600 °C. Oxygen lowered the onset temperature of thermal decomposition to 300 °C and led to complete decomposition at 600 °C. Three decomposition stages with temperatures of maximum decomposition rate at 320, 430, and 545 °C were observed. The first two decomposition stages with lower maximum decomposition temperatures are similar to those of fluorinated polyisoprene pyrolyzed under a nitrogen flow, and the third stage is the complete oxidative decomposition of the residue that was formed during the first two decomposition stages.

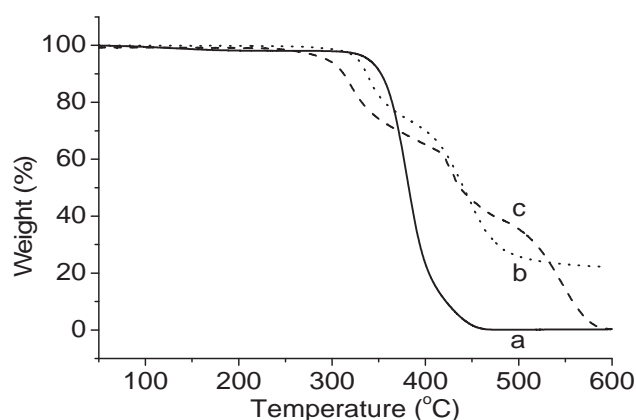
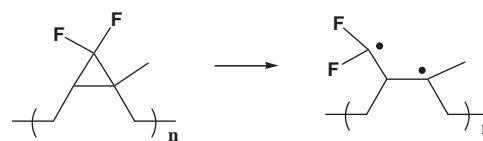


Figure 9. TGA curves of polyisoprene (a, solid line) and fluorinated polyisoprene under a nitrogen flow (b, dotted line), and an air flow (c, dashed line).



Scheme 3. The bond breakage of three-membered ring in fluorinated polyisoprene.

The lower onset decomposition temperature of fluorinated polyisoprene is attributed to the weak C–CF₂ bond in the three-membered ring structure and the formation of relatively stable free radicals (Scheme 3). These fluorine substituted free radicals are stabilized by the electronegative fluorine atoms, and the tertiary carbon free radicals are stabilized by *p-p* orbital resonance. The high steric tension in the three-membered ring and the formation of relatively stable free radicals all thermodynamically favor the bond breakage and trigger polymer decomposition.

The isothermal pyrolysis of fluorinated polyisoprene at 340 °C for 26 min led to a brown, insoluble material with 70–75 wt% of the starting mass (Figure 10). Below 200 °C, DSC characterization did not show an obvious glass transition. The elemental analysis showed relatively high carbon/hydrogen ratio and carbon/fluorine ratios for the pyrolyzed residues (Sample FC-py@340 in Table 2). Dehalogenation of fluorinated polyisoprene in isothermal pyrolysis is less than that of fluorinated PCHD because of the lower temperature of isothermal pyrolysis (340 vs 395 °C). Elemental analysis suggests that not only crosslinking but also dehalogenation occurred during the isothermal pyrolysis.

The FT-IR spectrum of the isothermally pyrolyzed residues (Figure 11b) shows the weakening of the C–F stretching (from 1100 to 1350 cm^{−1}) and the increasing C–H stretching on unsaturated carbons (3040 cm^{−1}) and the typical C=C–olefin stretching at 1700 (non-conjugated) and 1610 cm^{−1} (conjugated or

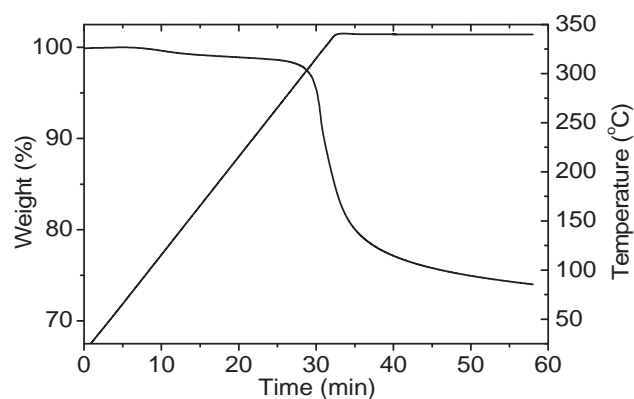


Figure 10. Isothermal pyrolysis of fluorinated PI (340 °C, 26 min).

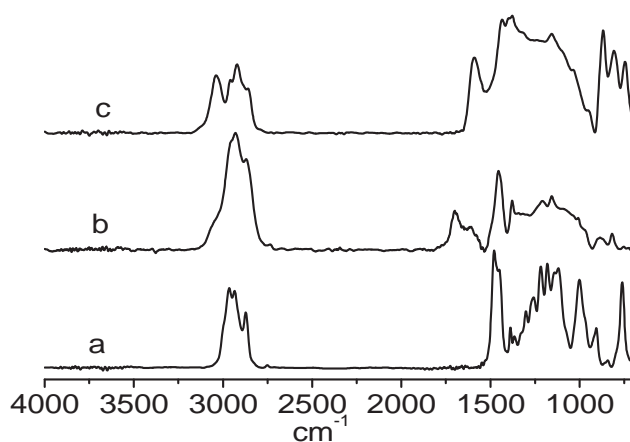


Figure 11. FT-IR spectra of fluorinated PI before (a), after pyrolysis at 340 °C, for 26 min (b) and heated to 600 °C (c).

aromatized), which indicate the formation of unsaturated, aromatized materials. Continuous pyrolysis at a higher temperature (up to 600 °C, Figure 11c) leads to a more aromatized structure, showing much stronger C–H stretching (3044 cm^{-1}) on unsaturated carbons, much stronger aromatized C–H out-of-plane deformation (745 , 810 , and 875 cm^{-1}), much stronger C=C stretching in aromatic style (1596 cm^{-1}) and the loss of non-conjugated C=C stretching (1700 cm^{-1}). The pyrolysis of fluorinated polyisoprene at high temperature (up to 600 °C) leads to a higher level of dehalogenation, dehydrogenation (Sample FC-py@600 in Table 2) and more aromatized black, graphite-like material, which exhibits a similar FT-IR spectrum and empirical formula to pyrolyzed fluorinated PCHD prepared via the same process.

4. Conclusion

Fluorination, by the addition reaction of in situ generated difluorocarbene, enhances the thermal stability of PCHD. The addition of difluorocarbene to double bonds results in a three-membered ring structure, which is degraded at high temperature because of the high ring strain and the polarity of the C–F bonds. The breakage of the ring structure triggers polymer decomposition through a two-stage decomposition process involving chain scission, free radical crosslinking, dehydrogenation, and dehalogenation. Fluorinated PCHD starts to decompose at relatively higher temperatures as compared with PCHD, but decomposes more thoroughly when held isothermally under the same conditions. Fluorinated polyisoprene starts to decompose at relatively lower temperatures as compared with polyisoprene, but forms thermally stable crosslinked structures while polyisoprene decomposes thoroughly under the

same conditions. Pyrolysis of fluorinated polydienes at high temperature leads to an unsaturated, aromatized, graphite-like carbon system, whereas polydienes are thoroughly decomposed to volatile materials over a narrow temperature and time range. The chemical modification of polydienes with fluorine not only increases thermal stability but also imparts unique physical properties (e.g., low dielectric constant, chemical resistance) as compared with hydrogenated polydienes.

Acknowledgements: The authors are grateful for financial support from U.S. Army Research Office (contract # W911NF-10-1-0282) and from the Division of Materials Science and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, under contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. K.H. acknowledges support from the Center for Nanophase Materials Sciences, which is sponsored at ORNL by Office of Science, US Department of Energy.

Received: October 2, 2011; Revised: November 7, 2011; Published online: December 14, 2011; DOI: 10.1002/macp.201100548

Keywords: fluoropolymers; degradation; glass transition; thermal properties; thermogravimetric analysis

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